

# A GEOCHEMICAL STUDY OF A MARSH ENVIRONMENT

*by*

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## INTRODUCTION

The study of the fate and distribution of carbon compounds and their associated trace elements in contemporary environments as well as ancient sediments has added information of importance to geology and the ocean sciences. These recent advances have been spurred on by such interests as the search for deposits of fossil fuels, the control of pollution, the understanding of the origins of life, the analysis of lunar samples, and the hopes for analyses of the surface of Mars.

The organic matter found in Holocene sediments is derived from once living organisms. The complex molecules synthesized by organisms and their degradation products are the object of study of organic geochemistry. After the death of an organism, most of the organic matter in it is utilized by other organisms or oxidized to  $\text{CO}_2$ . A small amount of the organic matter is not destroyed but is trapped in the top sediment. Biological activity gradually ceases, but slow chemical and physical transformations are continuous. Since the carbon-carbon bond is a strong bond, portions of the original molecules deposited in sediments often survive for long periods of time. Detection of many organic molecules in the concentrations found in nature was impossible before recent improvements in instrumental methods of separation, characterization and quantitation. With the present tools of mass spectrometry and gas chromatography the field of organic geochemistry has undergone a tremendous surge of activity.

The trace metal components of sediments provide a rich area for the study of geochemistry with such a diverse array of mechanisms responsible for their inclusion in the sedimentary environment. The biogenic source of trace metals in sediments is usually assumed but

rarely stimulates a great deal of interest. However, the biogenic component may play a significant role in trace metal fixation in highly productive areas. Because trace metals in a sediment may undergo radical changes in concentration levels with only slight changes in the overall chemistry of the sediment, they should be very sensitive indicators of certain microscale and macroscale chemical and biological factors in sedimentary environments. All organisms rely to a greater or lesser extent upon a constant supply of trace metals for the functioning of their metabolic processes. So profound is the need for certain trace metals in all organisms that they are termed essential trace metals whereas others may form an essential ingredient in the nutrients of only a few organisms. Others may perform no known function or be toxic to most organisms. Even so, plants and animals have the capacity to concentrate most trace metals from their environmental sources. When organisms die, most of the trace metals are released after decay, but a fraction may be retained in the organic debris trapped in the sediments and be preserved as a remnant of the pre-existing life forms. To study the trace metal transfer between sediments and plants, analytical tools of high sensitivity are required to cope with trace concentrations. Fortunately methods and instruments—particularly atomic absorption spectrophotometry—having the required sensitivity are available at modest costs to those interested in conducting trace metal analysis and have greatly facilitated this type of study.

Harbor Island, located approximately 1 mile north of Port Aransas, Texas (Fig. 1), was chosen as an environment to investigate in an organic and trace metal geochemical study. Situated at the head of Aransas Pass Channel, this tidal delta is characterized by a series of salt marshes inundated by tidal creeks and tidal channels. Maximum relief on the island is but 12 feet, but even slight variations in elevation are denoted by the variation of plant species dominating each zone of elevation. The plants are limited to the more hardy herbaceous species which withstand the extended periods of low rainfall and sediment dessication found in the intertidal and supratidal areas. Most of the identified species of plants are also native to the salt marshes of the off-shore islands of Mississippi. The fauna was restricted primarily to members of the lower phyla of the animal kingdom.

Several factors made this island ideally suited for geochemical investigations. The topography reveals rather simple and small scale physiographic processes. The island is protected both from effects of major oceanic disturbances by the barrier islands and from the effects of man by its relative inaccessibility. The minimal number of external parameters was helpful in facilitating the interpretation of the geochemical data collected.

The goal of this study was twofold: 1) chemically to characterize a specific salt marsh, the sediments and associated biota and 2)

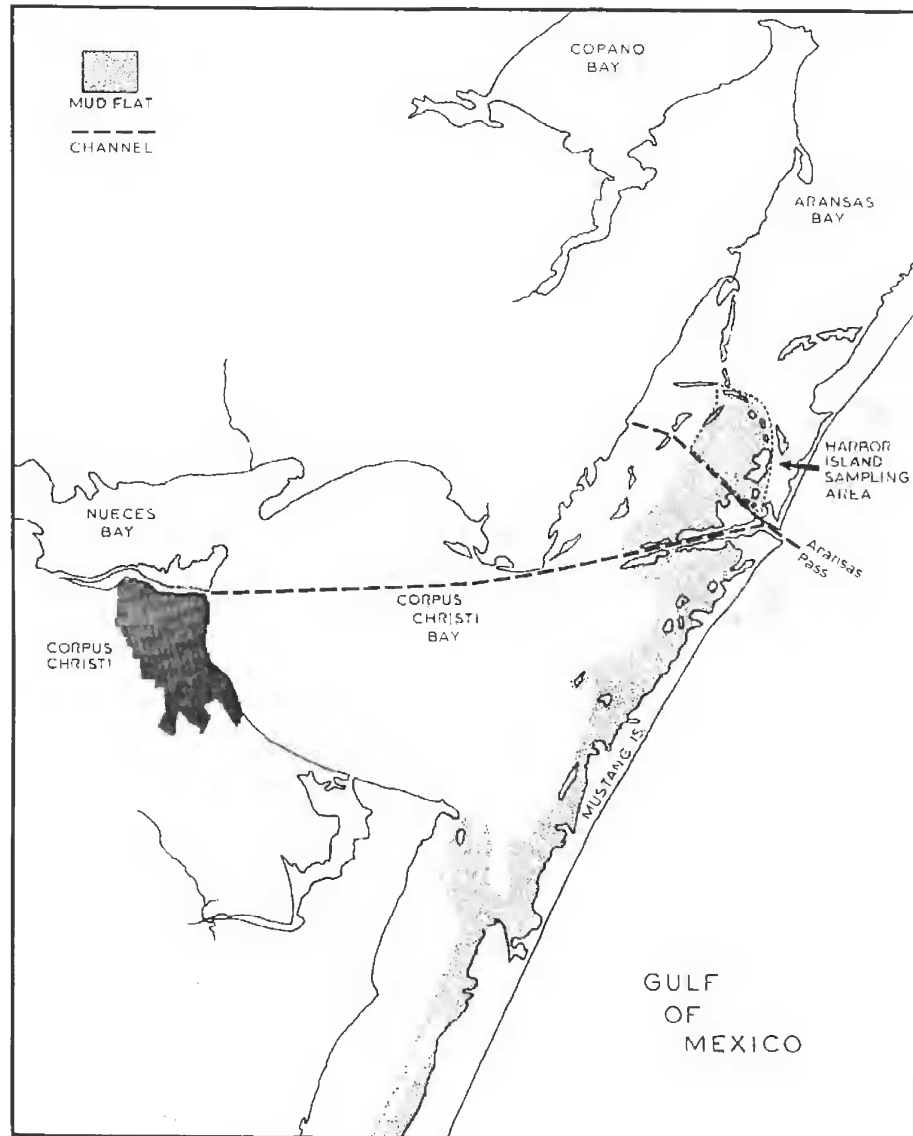


Figure 1. Map of collecting area.

to establish clear relationships between the chemical substances residing in the sediments and similar or identical substances occurring in the biological specimens.

In this particular study it was felt that the hydrocarbons would yield the most significant organic geochemical information. These compounds are ubiquitous but minor components of all organisms. Though their function is not entirely understood, it is known that they are concentrated in the waxy coatings of plants and most likely aid in the protective mechanisms of plants. Among the several classes of biochemical materials, the hydrocarbons exhibit probably the greatest resistance to biological and chemical degradation and therefore may be preferentially concentrated and preserved in sedimentary environments. An extreme variety of specific hydrocarbons occurs naturally in plants and hence the possible combinations and distributions of these hydrocarbons are limitless. The stability and unique distributions of hydrocarbons ranks them as a very important tool in the correlation of biolipids and geolipids.

In choosing the trace metals to be studied, preference was given to those that are known to be essential to all organisms. Those elements fitting this description were copper, zinc, molybdenum, manganese and iron. In addition cobalt known to be essential at least to blue-green algae was included. To monitor the biogenic contribution of non-essential trace metals, nickel, cadmium and lead were also analyzed in the samples. With the diverse functions of these various elements and occurrence at easily measurable levels in most organisms, they should provide useful information about the plant-sediment interplay in a salt marsh.

## EXPERIMENTAL

### *Collection and Handling*

A shallow depression outlined by a band of *Batis maritima* (Saltwort) and *Salicornia bigelovii* (Glasswort) was chosen as the site for sediment and plant collection for organic analysis. The sediments were black indicating a reducing environment and contained root motles and plant debris. Algal mats were forming at the edges of the depression and benthic organisms could be seen as they fed on detritus present at the surface. Sediment samples chosen for trace metal analysis were surface sediments from three intertidal zones of the island. In addition one subtidal, subsurface sample was taken from the littoral zone of the island. This latter sample was taken to define the trace element distribution in an area not influenced by the marsh plants.

For the organic analysis, seven marsh plants were collected, washed with distilled water and extracted immediately after collec-

tion. After washing the whole plants with distilled water to remove loose debris and epiphytes, the plants were minced in a Waring blender with methanol. The material was filtered and the methanol saved. The minced material was extracted ultrasonically for 15 minutes with 200 ml of chloroform with constant stirring. In addition to these seven plants, seven more species were collected for trace metal analysis (Table 1). Only herbaceous portions of the plants were saved. These

Table 1.  
Marsh Plants Analyzed

HYDROCARBONS AND TRACE METALS
<i>Limonium carolinianum</i> (Walt.) Britton (Sea lavender)
<i>Batis maritima</i> L. (Saltwort)
<i>Salicornia bigelovii</i> Torr. (Glasswort)
<i>Lycium carolinianum</i> Walt. (Christmas berry)
<i>Sesuvium maritimum</i> (Walt.) BSP (Sea Purslane)
<i>Oenothera drummondii</i> Hooker (Evening primrose)
<i>Borrichia frutescens</i> (L.) DC. (Sea ox-eyes)
TRACE METALS
<i>Spartina alterniflora</i> Loisel (Cord grass)
<i>Machaeranthera phyllocephala</i> (DC.) Shinnars
<i>Spartina patens</i> (Ait.) Muhl. (Salt-grass)
<i>Monanthochloe littoralis</i> Engelm. (Key-grass)
<i>Hedyotis nigricans</i> (Lam.) Fosberg
<i>Avicennia germinans</i> (L.) (Black mangrove)
<i>Distichlis spicata</i> (L.) Greene (Marsh spike-grass)

portions were quickly rinsed in double distilled water and oven dried at 60°C for 48 hrs. Following ashing in a muffle furnace at 450°C for 24 hrs., the samples were leached with 3N HCl and the filtrate over glass fiber filters was saved.

Sediment samples for all analyses were hand collected, and all necessary precautions were taken to eliminate contaminations and to arrest bacterial action. The sediment samples for hydrocarbon analysis were digested with dilute HCl to remove carbonates and washed to remove inorganic salts. Sediments for trace metal analysis were

oven dried at 60°C, weighed, ashed at 450°C digested in 3N HCl, filtered on glass wool and the filtrate saved.

The extracts from plants and sediments were further separated as follows:

### *Hydrocarbon Separation and Characterization*

Each lipid sample (plant and sediment) was saponified by refluxing with 0.5N KOH-MeOH for 1 hour. Nonsaponifiable components were removed by extracting the alkaline solution with benzene. Afterwards, the alkaline solution was acidified with dilute HCl to pH 3, and the fatty acids were extracted into benzene. Methyl esters of the fatty acids were prepared using  $\text{BF}_3$ -MeOH (Metcalf and Schmitz 1961). Silica gel (Woelm, Grade 200, Act. I) was packed beneath 25 ml alumina (Woelm Neutral, Grade 100, Act. I) in a 43 cm X 2.5 cm (o.d.) column. The nonsaponifiable residue was fractionated on the column into four parts: n-hexane fraction contained aliphatic hydrocarbons; benzene fraction contained aromatic hydrocarbons; chloroform-methanol (4:1, v/v) fraction contained alcohols; methanol fraction contained glycerides and the polar lipids.

The aliphatic hydrocarbons were identified and measured by gas chromatography on columns of SE-30, Apiezon L, and FFAP (Varian). Standard hydrocarbons were used to calibrate the Perkin-Elmer 880 gas chromatograph equipped with hydrogen flame ionization detectors. The columns were 8 feet by 1/8 inch o.d. copper tubing. The support was 80/100 mesh Chromosorb G, acid washed, dichlorodimethylsilane treated (Johns Manville). Fatty acid methyl esters were identified using the same instrument but using columns with FFAP, SE-30, and diethylene glycol succinate (DEGS). Linear-log plots of the retention times yielded straight lines for both hydrocarbons and acids and were useful for identification when standards for each carbon number were unavailable. Coinjection of standards were used to clarify some identifications. All hydrocarbon samples were run at programmed temperatures from 100° to 260° at 6°C per minute holding at 265°C. All fatty acid methyl esters were run from 150° to 265° at 6°C per minute holding at 265°C. Mass spectra were obtained with a modified Consolidated Electrodynamics Corp., Model 21-103C mass spectrometer. The spectra were run at 70eV.

Additional sample treatment helped in some identifications. Urea adduction enriched the branched from the nonbranched components. Sulfuric acid and/or bromine- $\text{CCl}_4$  treatment (Morrison and Boyd 1969) identified unsaturated component peaks.

The organic carbon content of the sediment was determined by a combustion technique using a Leco gasometric carbon analyzer.

### *Trace Metal Separation and Determination*

Iron was removed from the sediment filtrate by extraction of the iron-chloro complex from an 8N HCl solution of the total trace metals with isopropyl ether. Separation of all the trace elements of interest from matrix materials except Mo and Fe was effected by adjusting the pH to *ca* 3, adding sufficient ammonium pyrrolidine dithiocarbamate (APDC) to make the final solution 0.5% in APDC and extracting the APDC-metal complexes with methyl isobutyl ketone (MIBK). Molybdenum was extracted from a fresh batch of filtrate by adding KCNS and SnCl<sub>2</sub> to make a final 1N HCl solution 2% in both. The molybdenum-CNS complex was extracted with isopropyl ether.

All metals but molybdenum were analyzed using the Perkin-Elmer 303 atomic absorption spectrophotometer. The fuel was acetylene and the oxidant, compressed air. The MIBK solution of cobalt, cadmium, copper, manganese, nickel and zinc and the aqueous solution of iron were aspirated directly using the following wavelength settings (in nm): Cd-229, Co-241, Cu-325, Fe-248, Mn-279, Ni-232, Pb-283 and Zn-214. The color intensity of the Mo-CNS complex was measured at 460 nm on the Beckman Model DU spectrophotometer to determine molybdenum concentrations. Appropriate standards and blanks were prepared for all determinations and any necessary corrections were applied.

## RESULTS

### *Organic*

The hydrocarbons from the marsh plants and the blue-green algal mats were assumed to be the main source of the hydrocarbons for the ecosystem studied. Microorganisms were present, but their contribution is taken to be small in an organic-rich sink. Table 2 summarizes the analytical results.

Normal straight-chain hydrocarbons ranging from C<sub>15</sub> to C<sub>33</sub> were identified in the sediments. Pristane and phytane were present in low concentrations. Phytane was detected only in trace amounts. The branched hydrocarbons were only a very small percentage of the total hydrocarbon fraction. These branched hydrocarbons were almost completely olefinic.

The sediment hydrocarbon distribution was bimodal with maximums at C<sub>17</sub> and C<sub>29</sub> (Fig. 2). However, the largest concentration of hydrocarbons was in the C<sub>27</sub> to C<sub>31</sub> range. This reflects the hydrocarbon pattern found in the two prominent contributors to the organic matter, blue-green algae and higher plant life. Normal alkanes isolated from the marsh plants showed an odd-carbon number predomi-

Table 2.  
Marsh Plant and Sediment Analytical Analyses

Marine Plant	%	%	%	Major Component
	lipid dry wt	HC dry wt	HC lipid wt	
<i>Limonium carolinianum</i>	2.02	0.057	2.8	n-C29
<i>Batis maritima</i>	2.31	0.008	0.37	n-C27
<i>Salicornia bigelovii</i>	2.14	0.005	0.26	n-C31
<i>Lycium carolinianum</i>	3.41	0.085	2.3	n-C29
<i>Sesuvium maritimum</i>	1.91	0.005	0.32	n-C25
<i>Oenothera drummondii</i>	4.72	0.11	2.3	n-C29
<i>Borrchia frutescens</i>	4.91	0.043	0.75	n-C29
Sediment	0.15	0.0011	0.75	n-C29

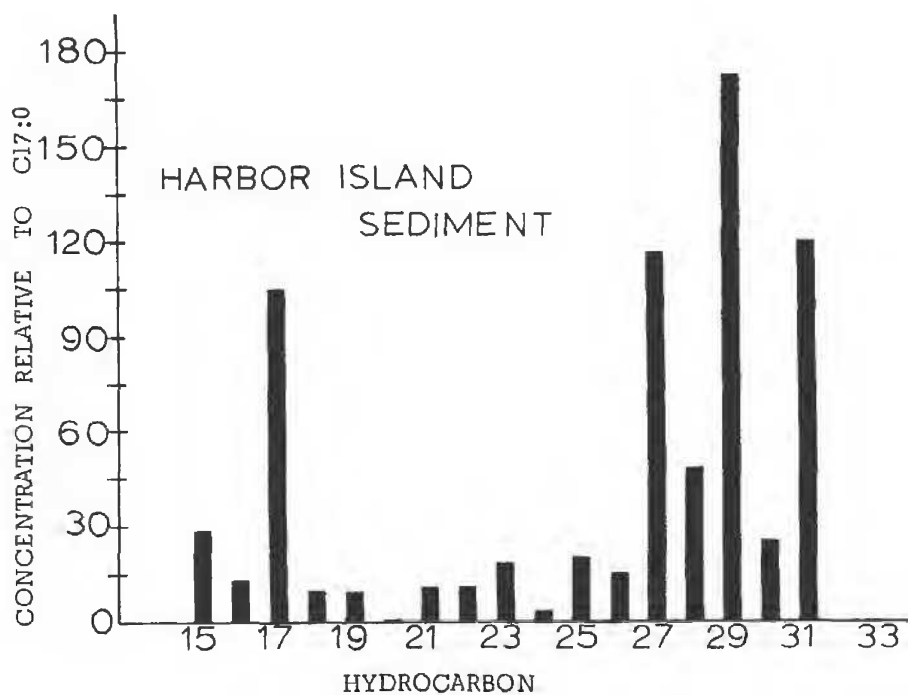


Figure 2. Histogram for normal hydrocarbons of Harbor Island sediments.

nance with C27, C29, and C31 the most prominent alkanes while C17 was the most prominent alkane in blue-green algae.

The urea adducted fraction of the hydrocarbons indicated that the cluster of peaks in the C18 range were not isoprenoid alkanes, but were branched-hydrocarbons with their branching points near the end of the chain. The large number of peaks in the C19 to C20 range were completely absent from the urea adducted fraction indicating that they were more highly branched. These peaks disappeared almost completely after treatment with  $H_2SO_4$ , indicating that they were olefinic.

Infrared spectra of urea adducted and urea nonadducted fractions confirmed the evidence that the olefins present in the sediment hydrocarbons are primarily multibranched olefins. In conclusion, the following generalizations can be made about the hydrocarbon results for the sediments analyzed:

- (1) All samples exhibited an odd-carbon preference.
- (2) A bimodal distribution was exhibited in the hydrocarbon patterns of sediments whose organic matter was derived from both blue-green algae and terrestrial plant sources.
- (3) The amount of extracted lipid material in plants was on the order of 25 times as great as that extracted from the sediments.
- (4) Pristane and phytane were found in all samples.

Normal alkane distributions in the plants were demonstrated between C13 and C35 but for the most part ranged between C23 and C31. Isoprenoid hydrocarbons, farnesane, pristane, and phytane, were identified, but this fraction represented less than 2% of the total fractions. Branched-chain hydrocarbons, *iso*-C27, C29 and C31, *anteiso*-C26, C28 and C30, were tentatively identified. There were some unidentified peaks in each chromatogram, but those peaks represented less than 10% of the total hydrocarbons. *Borrchia frutescens* contained a large number of branched and olefinic peaks in the C15 to C18 molecular weight range, none of which was identified (approximately 27% of the total hydrocarbons fell in this C15 to C18 range). In all other plants analyzed the lower molecular weight hydrocarbons represented less than 5% of the total weight.

There was a definite odd-carbon preference in every plant sample. The largest component in four of the species was C29. The distributions were slightly different for each species. Gas chromatographic analyses, tabulated in terms of individual normal hydrocarbons from C15 to C33, are presented in Fig. 3.

Olefins have been reported in the hydrocarbons of many plants (Stransky and Streibl 1969), but there was little evidence of olefins

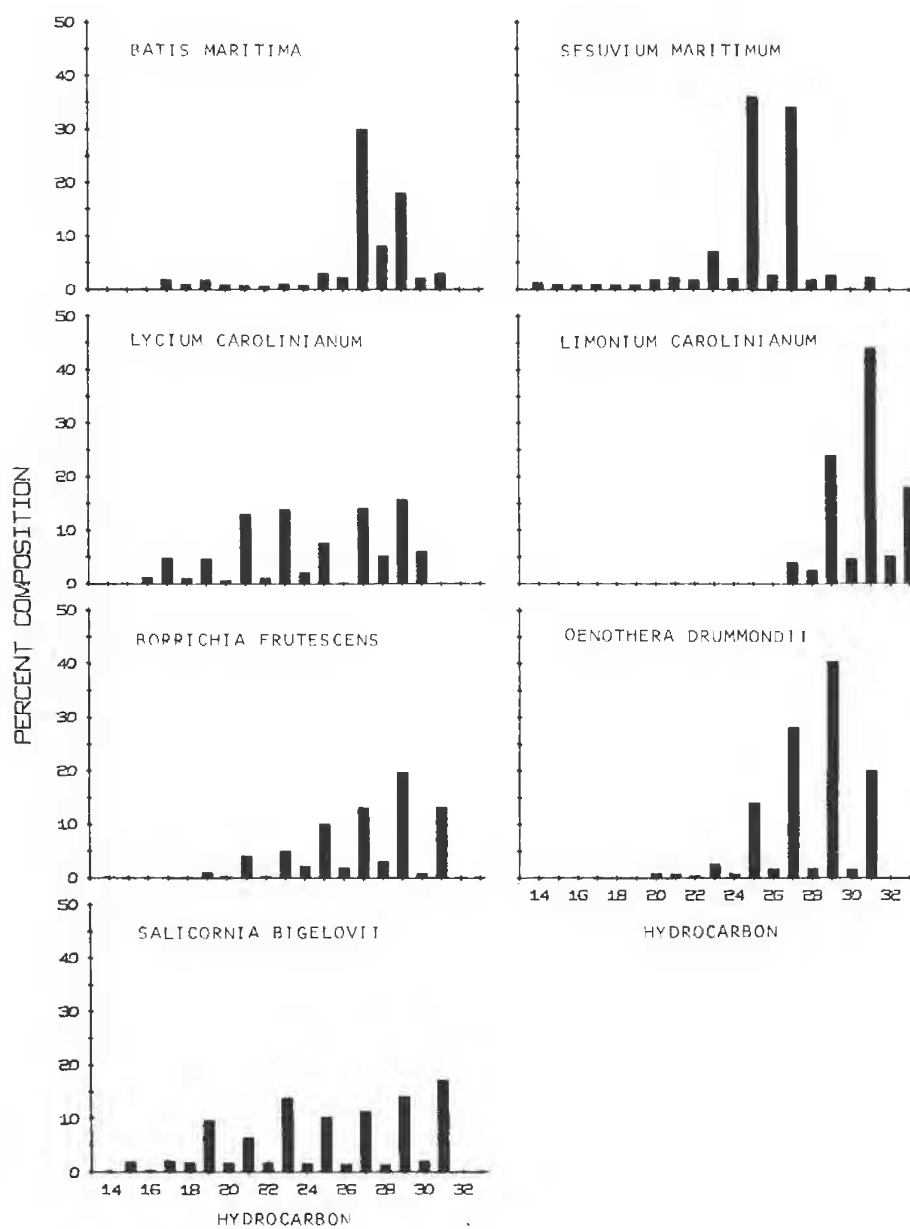


Figure 3. Histograms of normal hydrocarbons in marsh plants.

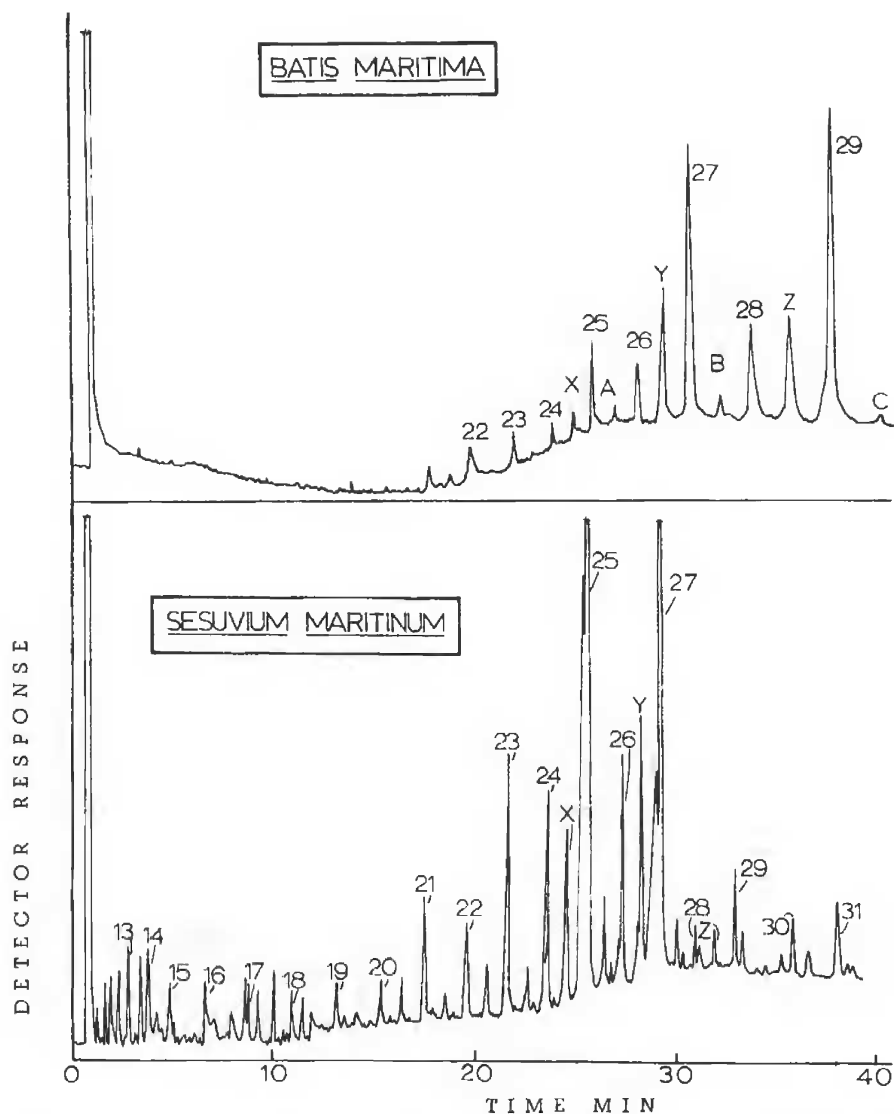
being present in greater than trace amounts in any sample except *Borrichia frutescens*. Microhydrogenation of olefins in this particular sample yielded normal alkanes. However, some peaks in this sample were not changed by hydrogenation; nor were they enriched in the urea nonadducted fractions. Hence, they were tentatively identified as branched hydrocarbons having their branching points near the end of the carbon chain.

Gas chromatograms are shown for two plants which contained unidentified peaks (Fig. 4). Tentative identification for the *iso*- and *anteiso*-alkanes as was given in Fig. 5 was based on their response to urea adduction, their inertness to  $H_2SO_4$ , and the absence of functional groups in the IR spectra. Plots of retention time *vs.* carbon number for the three series, normal alkanes, ABC, and XYZ yields three parallel lines which indicates that the latter series are two distinct, homologous alkane families.

### Trace Metals

In the sediments selected for trace metal analysis it was assumed that primary sources of biogenic material were the marsh plants. By choosing intertidal and supratidal sediments a large contribution from blue-green algae was hopefully excluded. A summary of the trace element data obtained from three surface and one subsurface sediments is contained in Table 3. Included are the results of organic carbon determinations. Overall the levels of trace metals are quite low when compared to an "average" sediment from the near-shore area such as provided by Chester (1965). The distribution among the sediments of any one element when compared to another shows similar trends so that it appears that no highly significant variations in trace metal fixations exist among the four sediments. However in inter-sediment comparisons it can be seen that significant differences do exist among the individual sediments, indicating degree rather than type as the more important aspect in investigating the effects responsible for trace metal fixation in these sediments.

The fourteen marsh plants have a trace metal distribution which is shown in Table 4. In Fig. 5 are displayed the ranges of trace metals in the marsh plants and some results of other workers in summarizing available data on terrestrial and on marine plants. Fitting certain characteristics of both groups, it might be expected that the marsh plants would assume some sort of "middle ground". These marsh plants appear to be slightly depleted in most elements except for molybdenum with respect to the terrestrial-marine range. With the principal source of heavy metals coming from the soil solution, it is not surprising from viewing the trace metal array in the sediments that these relatively low levels would be reflected in the biota of the regions.



**Figure 4. Chromatograms of *Batis maritima* and *Sesuvium maritimum* hydrocarbon extract:**

*Operating Conditions*

Column coating: FFAP  
Column dimensions: 150 ft.  
x 0.02 in

Temperature program: 150°-  
210° at 4°C/min  
Helium flow: 4 cc/min

*Key*

X-iso-C25	A-anteiso-C26
Y-iso-C27	B-anteiso-C28
Z-iso-C29	C-anteiso-C30

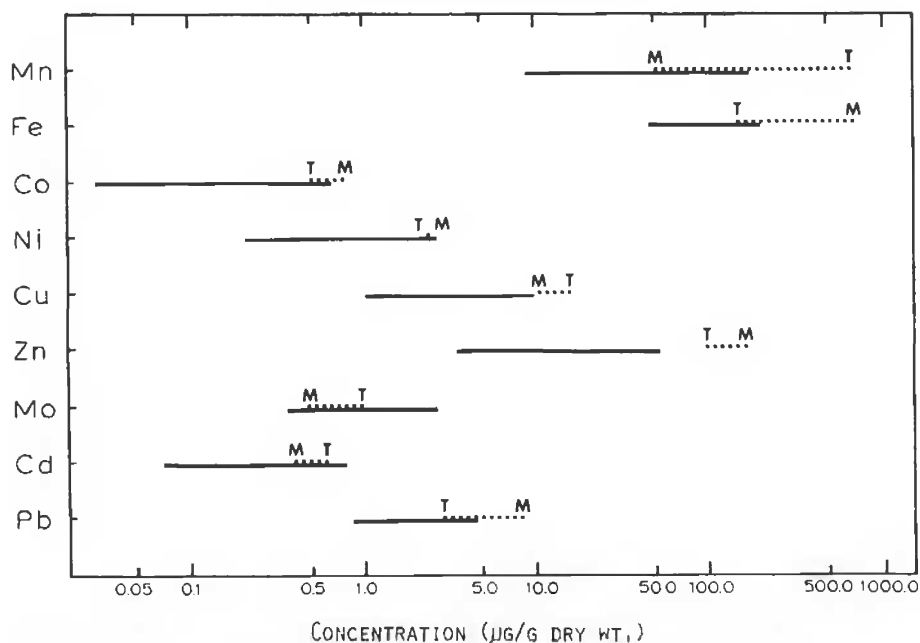


Figure 5. Ranges of trace metals in marsh plants—The range of each metal among the plants is indicated by the solid bar for that metal extending from the minimum value to the maximum value. Also included are bars extending from averages of terrestrial (T) to those of marine (M) plants reported by Bowen (1966).

## DISCUSSION

### *Hydrocarbons*

The odd-carbon predominance of the hydrocarbons in the Harbor Island sediments reflected the hydrocarbon composition of the marine plants, in particular the distribution in the C<sub>25</sub>–C<sub>31</sub> range. The large concentration of C<sub>17</sub> reflected the blue-green algal contribution to the sediment hydrocarbons (Winters, Parker and Van Baalen 1969, Gelpi et al. 1970). Thus, the correlation between biological and geological lipids was found to exist, the sediments retaining the biological information needed in order to recognize what type of life dominated their surroundings. This correlation between biological and geological hydrocarbons can be extended to include the isoprenoid hydrocarbons. Isoprenoids are abundant in the marine environment (Blumer 1965, Clark and Blumer 1967, Blumer, Mullin and Thomas 1964, Blumer and Thomas 1965). Pristane in marine algae was reported by Clark (1966). Pristane and phytane were found in photosynthetic and non-photosynthetic bacteria by Han et al. (1968). Isoprenoid hydrocar-

Table 3.  
Distribution of Trace Metals in Harbor Island Sediments

Sediment	Mn	Fe	Co	Ni	Cu	Zn	Mo	Cd	Pb	Org C
#1	108	0.96	5.0	10.9	5.2	28	n.d.*	1.11	3.6	0.66
#2	51	0.24	3.0	7.8	4.3	20	n.d.	0.61	9.0	0.31
#3	45	0.31	2.9	6.8	4.6	16	n.d.	0.42	3.4	0.22
#4	62	0.25	2.0	5.0	2.7	14	1.9	0.54	4.8	0.41
Avg. Std.										
Deviation(%)	11.6	1.9	3.2	5.0	6.9	2.8	-	9.6	6.1	-

Concentrations listed are expressed as  $\mu\text{g}$  metal/g dry-weight sediment except for Fe and organic C whose values are listed in wt. %.

The standard deviations for metal analysis by sediment are added and then averaged to arrive at the Average Standard Deviation.

\*n.d. - not detected.

Table 4.  
Distribution of Trace Metals in Harbor Island Marsh Plants

Plants	Mn	Fe	Co	Ni	Cu	Zn	Mo	Cd	Pb
<i>Salicornia bigelovii</i>	12	140	0.19	1.5	4.3	6.8	0.62	0.46	0.83
<i>Lycium carolinianum</i>	26	73	0.61	0.53	4.0	6.8	1.9	0.07	1.9
<i>Oenothera drummondii</i>	47	91	0.65	1.4	7.1	38	2.5	0.62	2.3
<i>Limonium carolinianum</i>	21	47	0.33	2.6	1.8	18	0.58	0.19	1.2
<i>Batis maritima</i>	27	200	0.27	1.6	3.3	30	0.36	0.13	1.3
<i>Borreria frutescens</i>	24	99	0.47	1.5	9.4	29	1.1	0.07	3.9
<i>Sesuvium maritimum</i>	15	49	0.13	0.89	2.8	3.4	0.36	0.19	1.3
<i>Spartina alterniflora</i>	41	90	0.14	0.85	2.8	17	1.6	0.35	3.3
<i>Machaeranthera phyllocephala</i>	24	55	0.066	0.88	5.4	50	1.6	0.57	1.6
<i>Spartina patens</i>	11	110	0.029	0.21	1.7	4.8	1.6	0.74	1.8
<i>Monanthochloa littoralis</i>	9.2	120	0.097	1.8	1.0	5.2	0.78	0.18	1.6
<i>Hedyotis nigricans</i>	18	98	0.12	1.5	5.2	42	1.8	0.40	3.0
<i>Avicennia germinans</i>	170	90	0.077	0.85	8.5	12	0.78	0.19	4.2
<i>Distichlis spicata</i>	22	82	0.061	1.2	2.3	20	2.0	0.14	1.8
Average Standard Deviation (%)	3.5	2.0	8.4	3.2	4.1	4.1	7.7	4.3	4.3

Concentrations listed are expressed as  $\mu\text{g}$  metal/g dry weight of plant.

The standard deviations for metal analysis by plant are added and then averaged to arrive at the Average Standard Deviation.

bons are found in petroleum and crude oils in very high concentrations (Bendoraitis, Brown and Hepner 1962, Han and Calvin 1969). The presence of only trace amounts of pristane and phytane in Harbor Island sediments indicates lack of pollution from these sources. This simple model should be useful. It could be of economic significance by its use in understanding the origin of fossil fuels. It could be of social significance by its use in understanding the fate of organic matter. With man's environment being polluted at a rapid pace, it is essential that we understand the fate of organic matter whether it be in the geosphere, atmosphere or hydrosphere if we are to gain control over our environment.

### Trace Metals

In an attempt to emphasize the fine differences in trace metal levels in the Harbor Island Sediments a plot of trace metal *vs* organic carbon was made and shown in Fig. 6. This selection of X-Y variables was made assuming the percentage organic carbon is a measure of biogenic input to the sediments. The trends and apparent deviations from these trends were observed rather than absolute levels to establish the correlation of organic matter and trace metal levels.

Since a slightly different selection of marsh plants prevail in each sediment area, a semi-quantitative estimate was made of the actual biomass of plant material in a 25-foot radius of the three surface sediments and the ratios of the various plants in those areas revealed the following plant contributors in decreasing order of importance:

Sediment No. 1—*Salicornia bigelovii*, *Batis maritima*, *Spartina alterniflora*, *Lycium carolinianum* (Christmas berry), *Limonium carolinianum*, *Borrchia frutescens* (Sea ox-eyes) and *Oenothera drummondii*.

Sediment No. 2—*Spartina alterniflora*, *Avicennia germinans* (Black mangrove), *Borrchia frutescens*, *Machaeranthera phyllocephala*, *Monanthochloe littoralis* (Key-grass), *Hedyotis nigricans*, *Distichlis spicata* (Marsh spike-grass) and *Spartina patens* (Salt-grass).

Sediment No. 3—*Salicornia bigelovii* and *Batis maritima*.

Defining the relationship of individual plants or groups of plants and the sediments for specific heavy metals was, in this limited study, impossible. However, by comparing the plant data to the data in Fig. 6 and observing the sediment-plant association groups some rather interesting information may be gained.

With respect to all elements but molybdenum (not shown in Fig. 6) a relative slump is seen in Sediment No. 4, the subsurface sample with little contribution from marsh plants. Still other effects such as

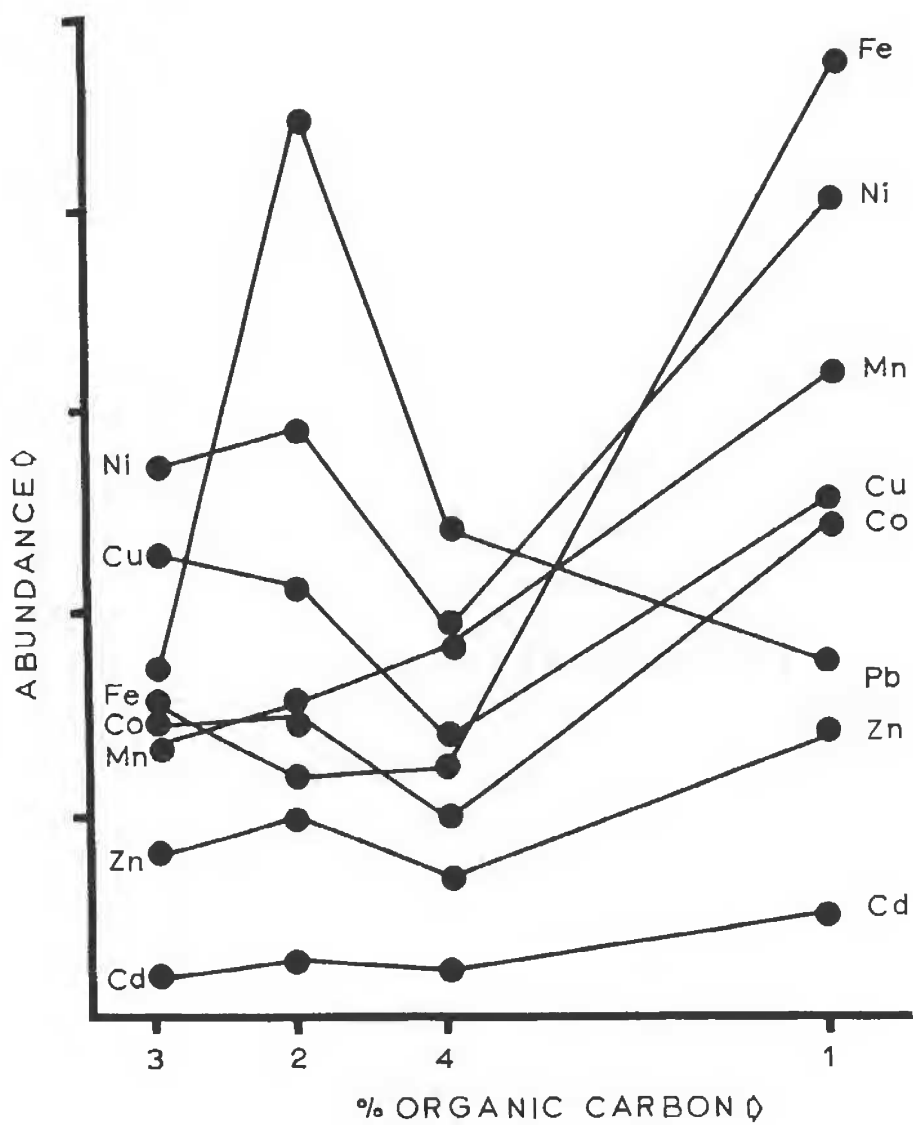


Figure 6. Metals *vs.* organic carbon in Harbor Island sediments—Numbers 1-4 on the organic carbon axis correspond to the Harbor Island soil sediment numbers from Table 3. Both ordinate and abscissa values are on a linear but arbitrary scale. Only the ordinate uses the origin as a value of zero. Organic carbon values: 1—0.66%, 2—0.31%, 3—0.22%, 4—0.41%.

migration of trace elements to the surface and concentration there is a known phenomenon and might account for the surface enrichment. It might be expected that this effect would be noticeable even in the absence of the marsh plants. To a degree the marsh plants still could contribute a significant portion of the trace metals. For any release by dissolution by bacterial action of trace metals beneath the surface of an intertidal or supratidal zone would certainly be impeded by the continual percolation downward of rainwater and receding tidal waters.

Most elements show a positive correlation with organic matter. This previously has been deduced by several workers (Jenne 1968). However, as Jenne pointed out, this contribution by organic matter acts really as a secondary effect. In sediments not having an overwhelming load of organic matter the organic matter with its trace metal load can establish the proper conditions for inclusion of trace metals in ferromanganese oxides. These oxides present in most oxidizing sediments are known to act as very effective trace metal accumulators. The marsh plants may not complete the fixation of trace metals in sediments but at least may start the process by acting as a source and sediment conditioner.

Iron appears quite enriched in Sediments No. 1 and 3 relative to Sediments No. 2 or 4. It seems that any explanation based on a physiological or geological basis would also alter the distribution of other elements more so than observed. It could very well be that the marsh plants are more active in the transport of this element than the others. Neither Sediment No. 2 nor 4 received any sizeable contribution from *Salicornia bigelovii* or *Batis maritimum* or others having the highest concentrations of iron. Baas Becking and Moore (1959) concluded that the majority of iron in marine sediments exists as complexed iron so that it is possible that these two plants supply substantial amounts of complexed iron in their plant litter.

Though molybdenum is extremely depleted in the surface sediments (Table 3), this metal maintains a normal level in the subsurface sediment. In the marsh plants the levels of molybdenum are the only ranges above and including those predicted from averages of terrestrial and marine plants (Fig. 5). It is known that in surface, oxidizing sediments molybdenum may be lost through its conversion to the soluble molybdate ion whereas in subsurface reducing sediments molybdenum as well as copper, iron, zinc et al. may be retained as their insoluble sulfides. The marsh plants then must speed the depletion of molybdenum from surface samples which after decay of the plants is either leached out of the sediments or transported to reducing layers deeper in the sediments.

Lead is greatly enriched in Sediment No. 2. Some of the plants in this area contain the highest levels of lead though their relative enrichment over those species in other areas could not fully account for

this high level. The possibility of some lead or other metal contamination cannot be entirely dismissed in view of the debris washed in by tidal action.

The marsh plants as a whole have exhibited an ability about as strong as terrestrial and marine plants in accumulating a variety of trace metals from their environment. In some cases the marsh plants may act as sources for trace metal enrichment in the sediments and in other instances, notably molybdenum, as an active depleting agent. The coastal marsh environment widespread along the Gulf and Atlantic coastlines will undoubtedly continue to be a primary target of heavy metal pollution. The varying degrees of enrichment of the various elements both essential and nonessential in marsh plants should make them of value in establishing base-line evaluations of heavy metal inventories in a coastal area.

#### LITERATURE CITED

- Baas Becking, L. G. M. and D. Moore. 1959. The relation between iron and organic matter in sediments. *J. Sediment. Petrol.* 29:454.
- Bendoraitis, J. G., B. L. Brown and L. S. Hepner. 1962. Isoprenoid hydrocarbons in petroleum. *Anal. Chem.* 34:4.
- Blumer, M. 1965. Organic pigments: their long-term fate. *Science* 149:722.
- Blumer, M., M. M. Mullin and D. W. Thomas. 1964. Pristane in the marine environment. *Helgolander wiss. Meeresunters* 10:187.
- Blumer, M. and D. W. Thomas. 1965. Phytadienes in zooplankton. *Science* 147:-1148.
- Bowen, H. J. M. 1966. *In* Trace Elements in Biochemistry, Academic Press, New York.
- Chester, R. 1965. Elemental geochemistry of marine sediments. *In* Chemical Oceanography Vol. 2, (editors, J. P. Riley and G. Skirrow), Academic Press.
- Clark, R. C., Jr. 1966. Master's thesis, Woods Hole Oceanography Institution, Woods Hole, Mass.
- Clark, R. C. and M. Blumer. 1967. Distribution of paraffins in marine organisms and sediment. *Limnology and Oceanography* 12:79.
- Gelpi, E., H. Schneider, J. Mann and J. Oró. 1970. Hydrocarbons of geochemical significance in microscopic algae. *Phytochemistry* 9:603.
- Han, J. and M. Calvin. 1969. Occurrence of C<sub>22</sub>-C<sub>25</sub> isoprenoids in Bell Creek crude oil. *Geochim. Cosmochim. Acta* 33:733.
- Han, J., E. D. McCarthy, M. Calvin and M. H. Benn. 1968. Hydrocarbon constituents of the blue-green algae *Nostoc muscorum*, *Anacystis nidulans*, *Phormidium luridum* and *Chlorogloea fitchii*. *J. Chem. Soc. (Sect. C)*, 2785.
- Jenne, E. A. 1968. Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. *In* Trace Inorganics in Water, American Chemical Society, Washington.
- Metcalfe, L. D. and A. A. Schmitz. 1961. The rapid preparation of fatty acid esters for gas chromatographic analysis. *Anal. Chem.* 33:363.
- Morrison, T. R. and R. N. Boyd. 1969. *In* Organic Chemistry, 2nd Ed. Allyn and Bacon, Inc., Boston.
- Stransky, K. and M. Streibl. 1969. On natural waxes. XII. Composition of hydrocarbons in morphologically different plants. *Collection Czeskoslov. Chem. Commun.* 34:103.
- Winters, K., P. L. Parker and C. Van Baalen. 1969. Hydrocarbons of blue-green algae: geochemical significance. *Science* 163:467.